

Preparation of Silver-Montmorillonite Nanocomposites by Reduction with Formaldehyde and Borohydride

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Montmorillonite rica em sódio (MMT) foi intercalada com cátions prata, os quais foram subsequentemente reduzidos com formaldeído ou boroidreto de sódio. Os nanocompostos prata-montmorillonite foram estudados por espectrometria UV-Vis, microscopia eletrônica de transmissão (TEM) e difratometria de raios-X (XRD). A influência de diferentes agentes redutores na dispersão e no tamanho das partículas de prata depositadas na superfície da montmorillonite foi investigada. A redução com boroidreto produziu partículas de prata dispersas uniformemente, com tamanhos limitados entre 3 e 13 nm. A redução com formaldeído gerou partículas dispersas irregularmente com uma distribuição de tamanho muito maior, variando entre 3 e 100 nm. Além disso, entre as partículas de prata preparadas por redução com formaldeído, algumas partículas de Ag₂O foram obtidas como resultado de redução incompleta. Os compósitos de prata-montmorillonite preparados por redução com boroidreto e formaldeído contêm 2,4% e 5,3% em massa de Ag, respectivamente.

Na-rich montmorillonite (MMT) was intercalated with silver cations, which were subsequently reduced with formaldehyde or sodium borohydride. The silver-montmorillonite nanocomposites were studied by UV-visible spectrometry, transmission electron microscopy (TEM) and X-ray diffractometry (XRD). The influence of different reducing agents on the dispersity and size of silver particles deposited on montmorillonite surface was investigated. The reduction with borohydride gives rise to uniformly dispersed silver particles with a narrow particle size distribution from 3 nm to 13 nm. Formaldehyde reduction forms unevenly dispersed particles with a much wider size distribution, ranging from 3 to 100 nm. In addition, some Ag₂O particles were found among silver particles prepared with formaldehyde, likely as a result of incomplete reduction. Silver-montmorillonite composites prepared by reduction with borohydride and formaldehyde contain 2.4 wt% and 5.3 wt% of Ag, respectively.

Keywords: silver, nanocomposites, montmorillonite, reduction, formaldehyde, borohydride

Introduction

Silver nanocomposites are used for many industrial applications, such as resonant and nonlinear optical elements, high-dielectric strength media for capacitors, enhanced electrical conductivity of ceramic media, pattern etching using HF, augmentation of electrode response, magnetic spin glasses, etc. A variety of conventional sol-gel preparation methods exists for Ag-nanocomposites fabrication, either as bulk powder or thin films, using organically modified gels or gel precursors.^{1,2} Another

type of Ag-nanocomposites are silver nanoparticles deposited on inorganic platforms, such as Al₂O₃, SiO₂, SiO₂/B₂O₃, SiO₂/TiO₂, TiO₂, BaTiO₃, etc.¹ Phyllosilicates, such as montmorillonite²⁻⁴ and kaolinite,⁵ have been also used as carriers for silver particles.

For the preparation of Ag-nanocomposites, silver nitrate is often used as the primary source of silver ions. There are several ways of Ag⁺ reduction: use of gamma,⁶ UV,⁷ or femtosecond laser irradiations,⁸ heating,⁹ electrochemical reduction,¹⁰ application of reducing chemicals, such as hydrazine,¹¹ sodium borohydride,⁵ glycerol,^{3,12} *N,N*-dimethylformamide,¹³ glucose,¹⁴ ethylene glycol,⁴ formaldehyde,^{15,16} sodium in liquid ammonia,¹⁷ etc. In

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addition, reduction of $[\text{Ag}(\text{NH}_3)_2]^+$ by various saccharides was described by Panáček *et al.*¹⁸

The aim of this work was to prepare a temperature-stable silver nanocomposite consisting of silver nanoparticles deposited on an inorganic carrier. For this purpose, silver ions were adsorbed on montmorillonite (MMT) and reduced by borohydride or formaldehyde. The size and dispersity of silver particles located on the phyllosilicate surface were studied. The development of methods for the preparation of silver nanoparticles of required diameter ranges is desired.

Experimental

Nanocomposite preparation

Reagents

All chemicals were of analytical reagent grade: formalin (37%), sodium hydroxide, triethanolamine (TEA), sodium bicarbonate (Lachema, Czech Republic) and sodium borohydride (NaBH_4 , Merck, Germany). Water used for the preparation of solutions was deionised by reverse osmosis.

Adsorption procedure

Na^+ -rich montmorillonite SWy 2 (Crook County, Wyoming) with exchange capacity of 1.2 mequiv g^{-1} , determined by saturation with NH_4^+ ¹⁹ and by analysis of released metals (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), was used for the adsorption of silver cations. The MMT formula is $\text{Na}_{0.38}\text{K}_{0.04}(\text{Ca}_{0.12}\text{Mg}_{0.50}\text{Fe}^{3+}_{0.41}\text{Al}_{2.90}\text{Ti}_{0.01}\text{Mn}_{0.01})\text{Si}_8\text{O}_{20}(\text{OH})_4$, as calculated from the results of X-ray fluorescence analysis. A fraction of MMT (particle size $< 5 \mu\text{m}$) separated by sedimentation was used.

The adsorption procedure was adopted from our recent work.² A portion of MMT (about 0.1 g) was added into 100 mL of 0.010 mol L^{-1} AgNO_3 solution and this suspension was shaken vigorously for 24 h. The suspension was then centrifuged (4500 min^{-1}) for 20 min, filtered through 1.2 μm glass fibre filters (Whatman), and dried gently at 50 °C for 24 h. All experiments were performed at room temperature varied from 20 °C to 24 °C. Montmorillonite containing silver ions is labelled Ag^+ -MMT.

Reduction procedure

Two procedures for silver reduction were tested: the reduction with formaldehyde and the reduction with NaBH_4 . Formaldehyde reduction consisted of the following steps: (i) 10 mg of Ag^+ -MMT were placed into a test tube, (ii) 5 mL of 0.37% formaldehyde solution and (iii) 0.5 mL of alkaline reagent (NaOH , NaHCO_3 , TEA) were added,

and the suspension was mixed and shaken. For the reduction with NaBH_4 , 10 mg of Ag^+ -MMT were placed into a test tube and 5 mL of NaBH_4 solution (0.010 mol L^{-1}) were added and shaken.² This reaction is vigorous and takes only several min. Ag -MMT suspensions were analysed by UV-visible spectrometry.

After reduction, Ag -MMT was filtered out through 1.2 μm glass fibre filters and washed several times with water to remove residual Ag^+ ions, which were then analysed in the filtrates by silver electrode (Theta 90, Czech Republic). Silver was also analysed in the filtrates, after dissolution with HNO_3 , by atomic absorption spectrometry (see below). Silver particles adsorbed on MMT were further studied by transmission electron microscopy and X-ray powder diffraction.

Ag -montmorillonite composites prepared with borohydride were labelled as Ag -MMT/ NaBH_4 , while those prepared with formaldehyde were labelled as Ag -MMT/F. The products of reduction with formaldehyde were also labelled as F- NaOH , F- NaHCO_3 and F-TEA, depending on the alkaline reagent used.

Characterization methods

UV-visible absorption spectrometry

UV-visible absorption spectra were measured with a Lambda 25 double-beam spectrometer (Perkin Elmer, USA). All spectra were recorded using 1 cm quartz cuvettes within the range of 200 nm to 800 nm. The cuvettes were filled with shaken suspensions and the spectra of MMT, Ag^+ -MMT and Ag -MMT were recorded immediately against distilled water.

Atomic absorption spectrometry

An atomic absorption spectrometer Spectra AA30 (Varian Inc., USA) was used for the determination of silver in the filtrates using a standardised method.²⁰ Air-acetylene flame was employed as the atomisation technique.

Transmission electron microscopy

Transmission electron microscopy analysis was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB₆ cathode, point resolution 0.17 nm) with an EDX (Energy Dispersive X-ray) detector attached. Images were recorded on a CCD camera with the resolution of 1024 × 1024 pixels using the Digital Micrograph software package.

Powder samples were dispersed in ethanol and the suspension was treated with ultrasound for 10 min. A drop of a very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry by evaporation at room temperature. Selected-area electron diffraction

(SAED) patterns were analyzed using the Process Diffraction software package.²¹

X-ray powder diffraction

The X-ray powder diffraction study was performed using a powder diffractometer INEL CPS 120 (INEL, France) equipped with a curved position-sensitive detector PSD 120 MB/11 (reflection mode, Ge-monochromatized, Cu-K_{α1} radiation), which allows simultaneous data collection over 0° to 120° with steps of 0.031° in 2-theta. The diffraction patterns were acquired in ambient atmosphere under constant conditions (2000 s, 35 kV, 20 mA).

Statistical software

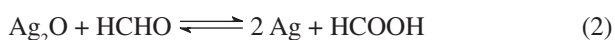
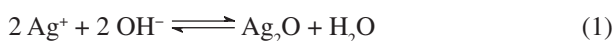
All statistical calculations were made at $\alpha = 0.05$ significance level by the program QC.Expert 2.5 (Trilobyte Statistical Software, Ltd., Czech Republic).

Results and Discussion

In the first step of nanocomposite preparation, silver cations were adsorbed on montmorillonite (Ag⁺-MMT) by shaking in AgNO₃ solution for 24 h. Thereafter, Ag⁺-MMT was filtered out and dried, and silver cations were reduced by addition of aqueous solutions of formaldehyde or sodium borohydride.

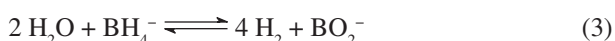
Reduction of silver ions

The reduction with formaldehyde is described by the following reactions:^{14,22}



Alkaline conditions, which are essential for reaction 1, were provided by addition of sodium hydroxide, sodium bicarbonate or triethanolamine (TEA).

The reduction with borohydride consists of (i) *in-situ* generation of hydrogen by the decomposition of NaBH₄ and (ii) reaction of hydrogen and silver ions:²



No other additives are necessary. Ag-MMT composites were separated from the dispersions by filtration (see

Experimental). The efficiency of the reduction was determined by electrochemical analysis of residual silver cations in the filtrates with a silver electrode. The limit of quantification (LOQ) of the method was estimated at $1 \times 10^{-6} \text{ mol L}^{-1}$ of Ag⁺, which corresponds to 0.02 wt% of silver in Ag-MMT. The concentrations of residual Ag⁺ were lower than LOQ in all filtrates. It corresponds to a reduction efficiency $\geq 99.98\%$.

The content of silver in each Ag-MMT composite was determined by AAS after its dissolution in a mixture of HF, HNO₃ and HClO₄ (5:4:4).²³ The reproducibility of the Ag-MMT preparation was estimated at 2.6%. The amount of Ag in Ag-MMT significantly depends on the reducing reagent used. While using borohydride, 2.4 wt% Ag (0.22 mmol g⁻¹) was found. The content of Ag formed by formaldehyde was similar in all Ag-MMT samples regardless of the employed alkaline agent, *i.e.*, 5.3 wt% (0.49 mmol g⁻¹). This difference is given by the size of silver particles. Small Ag particles of Ag-MMT/NaBH₄ probably passed through the filter pores into the filtrates in higher amounts than those of Ag-MMT/F. This was also confirmed by TEM (see below) and by analysis of Ag in the filtrates. A higher content of Ag in Ag-MMT should be achieved by filtration through denser filters.

UV-visible absorption study

It is well known that the surface plasmon of silver nanosized particles exhibits a characteristic adsorption band around 410 nm. Therefore, the optimal reaction time and concentrations of all reagents could be tuned by recording the UV-visible absorption spectra of Ag⁺-MMT suspensions.

The initial concentrations of NaOH and NaHCO₃ were 0.010, 0.050, 0.10, and 0.20 mol L⁻¹. Solutions of TEA had concentrations of 0.010, 0.050 and 0.10 mol L⁻¹. UV-visible spectra were measured after 0.5, 1, 2, and 4 h. Absorbance was measured at the absorption band maxima (λ_{max}).

Graphs showing the changes of absorbance *versus* reaction time are shown in Figures 1a-c. In the case of formaldehyde, the absorbance increases during the first two hours and then stays nearly constant. Therefore, two hours were selected as the sufficient reaction time for the quantitative reduction. The optimum concentrations of the bases were chosen so that the highest reduction efficiency, expressed by the highest absorbance around 410 nm, was reached: 0.10 mol L⁻¹ for both NaOH and NaHCO₃, and 0.50 mol L⁻¹ for TEA. At the higher concentrations, the absorption band becomes lower and broader. The optimum conditions for the reduction with borohydride (0.01 mol L⁻¹) have been studied recently.²

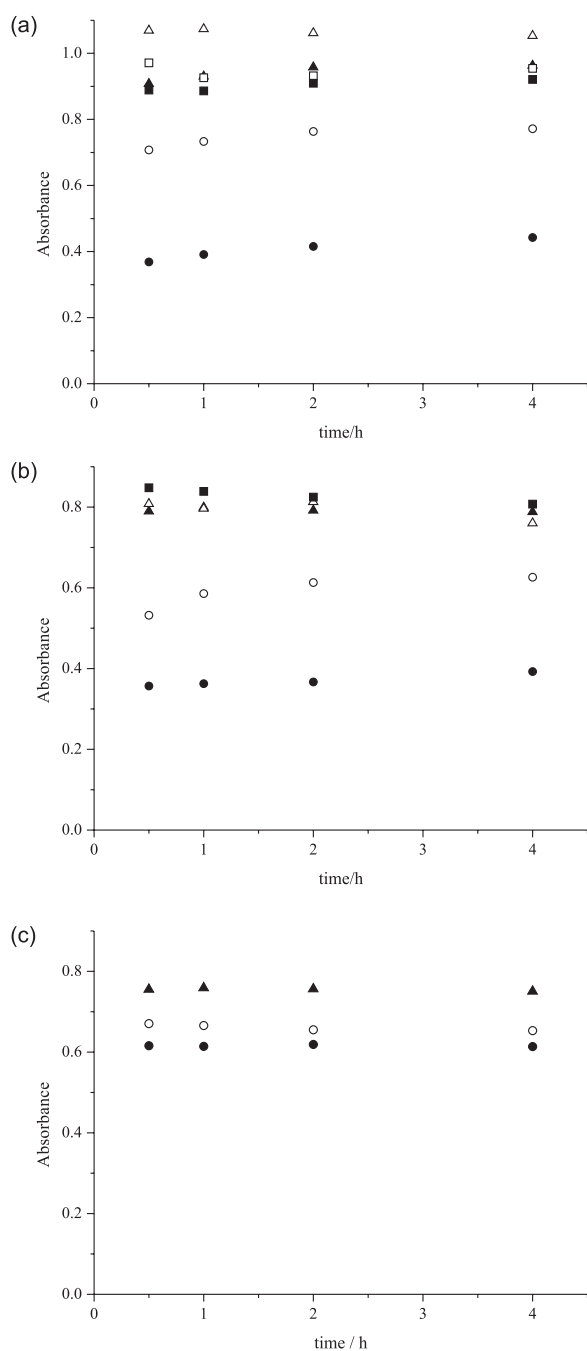


Figure 1. (a) Time dependence of silver plasmon absorbance after the reduction with formaldehyde using NaOH: (●) 0.010 mol L⁻¹, (○) 0.050 mol L⁻¹, (▲) 0.10 mol L⁻¹, (△) 0.20 mol L⁻¹, (■) 0.30 mol L⁻¹, and (□) 0.40 mol L⁻¹; (b) time dependence of silver plasmon absorbance after the reduction with formaldehyde using NaHCO₃: (●) 0.010 mol L⁻¹, (○) 0.050 mol L⁻¹, (▲) 0.10 mol L⁻¹, (△) 0.20 mol L⁻¹, (■) 0.50 mol L⁻¹; (c) time dependence of silver plasmon absorbance after the reduction with formaldehyde using TEA: (●) 0.05 mol L⁻¹, (○) 0.10 mol L⁻¹, (▲) 0.50 mol L⁻¹.

UV-visible absorption spectra

The absorption spectra of silver particles are presented in Figure 2. The absorption maximum corresponding to borohydride reduction occurs at wavelength

λ_{\max} ca. 400 nm. The absorption maxima related to formaldehyde reduction are shifted to longer wavelengths depending on the base employed: λ_{\max} ca. 412 nm for NaOH and TEA, λ_{\max} ca. 425 nm for NaHCO₃. The shifts in the λ_{\max} of the silver plasmon to longer (red shift) and shorter wavelengths (blue shift) have already been described in the literature.^{22,24,25} There are several reasons for these effects: electron density on the surface of nanoparticles, irregular shape and size of nanoparticles, media constants of solutions, refraction coefficients, etc.

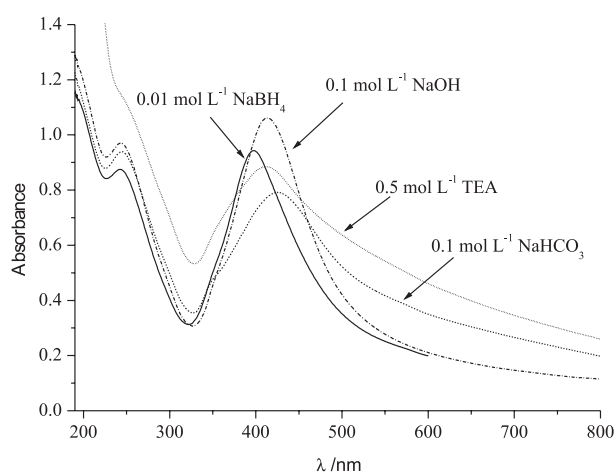


Figure 2. UV-visible absorption spectra of silver particles produced under different conditions.

Besides the shifts, broadening of the plasmon peak was also observed, which is in agreement with the findings of other authors.^{11,16} Such broadening might be caused by the aggregation of silver particles. The narrowest peak belongs to silver particles reduced by NaBH₄. The other silver peaks become broader in accordance with the alkaline agents used in combination with formaldehyde: NaOH < TEA < NaHCO₃.

In addition, there is a band at about $\lambda_{\max} = 250$ nm in the absorption spectra (Figure 2), which most likely originates from light scattering on montmorillonite particles. The absorption band at around 300 nm, which has been attributed to residual Ag⁺ ions¹⁴ or to the existence of Ag nanoparticles smaller than 2 nm,²⁵ was not found at all.

Based on the data mentioned above, the following can be said. Borohydride reduction is much faster than that by formaldehyde, and thus silver particles are expected to be smaller, as indicated by the narrower absorption peak and the shorter λ_{\max} . As the concentration of formaldehyde was identical in all experiments, the concentration of hydroxide ions should be a key parameter for the formaldehyde reduction rate (see reactions 1 and 2). Taking into account the strength of the bases (TEA with pK_b = 6.24 and NaHCO₃

with $pK_b = 7.65$), the concentration of hydroxide ions in the aqueous solutions of the weak bases can be estimated from the well-known equation: $pOH \approx 0.5 (pK_b - \log c_B)$, where c_B is the concentration of the weak base. The calculated concentration of OH^- ions, c_{OH^-} , decreases in the order: $NaOH (c_{OH^-} \approx 10^{-1} \text{ mol L}^{-1}) > TEA (c_{OH^-} \text{ ca. } 10^{-3.3} \text{ mol L}^{-1}) > NaHCO_3 (c_{OH^-} \approx 10^{-4.3} \text{ mol L}^{-1})$, which is consistent with the order of absorption band broadening. For comparison, λ_{max} values increase in the order: $NaBH_4 < NaOH \approx TEA < NaHCO_3$. Therefore, it can be assumed that the size of silver particles increases in the order $NaBH_4 < NaOH < TEA < NaHCO_3$. The particles diameter and their dispersity were further investigated by TEM.

TEM study

TEM micrographs of silver particles deposited on montmorillonite surface are shown in Figure 3, together with the corresponding SAED patterns as insets. In the SAED patterns, which are compared to the XRD diffraction patterns in Figure 4, crystalline cubic Ag and montmorillonite were detected. The apparent miss of non-basal peaks of montmorillonite in SAED against XRD is due to the strongly preferred orientation of montmorillonite in TEM samples, which were prepared by sedimentation from suspension. The diffraction peaks of Ag are not well defined, which suggests a number of structural defects.

In addition, a diffraction peak corresponding to AgO/Ag_2O was observed in the sample $Ag\text{-MMT}/F\text{-}NaHCO_3$,

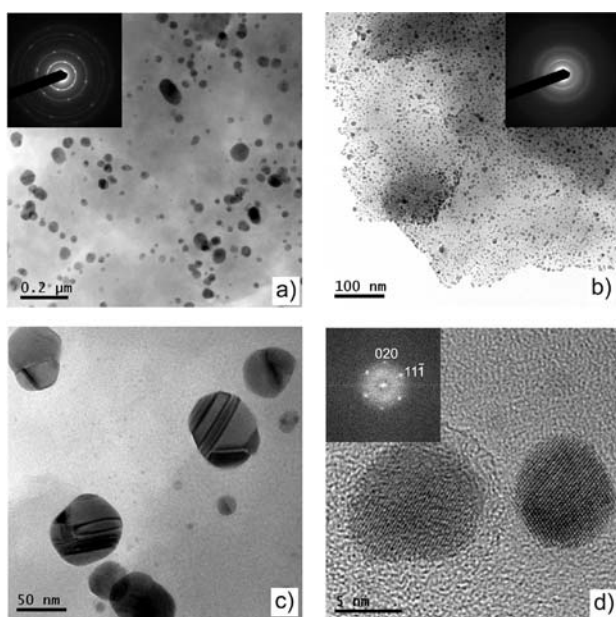


Figure 3. TEM micrographs of silver particles on montmorillonite. (a) Ag particles prepared by reduction with F-NaOH, (b) $NaBH_4$, (c) twinning of Ag particles prepared by reduction with F-NaOH, (d) Ag crystal along [101] in $Ag\text{-MMT}/F\text{-}NaHCO_3$.

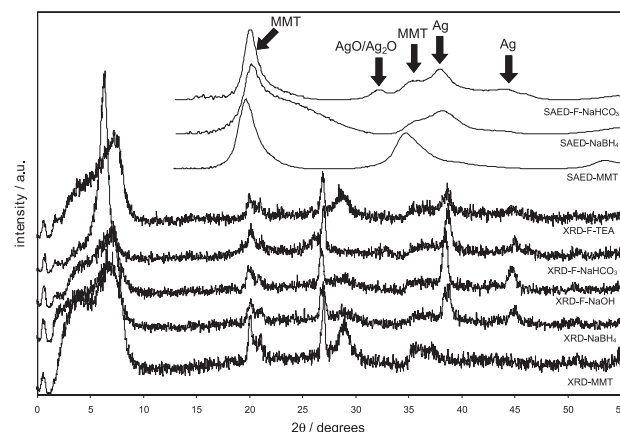


Figure 4. XRD and SAED patterns of $Ag\text{-MMT}$ nanocomposites.

This peak very likely indicates the presence of Ag_2O as a result of incomplete reduction according to reaction 2. The fact that the oxide is not found in the SAED patterns of $Ag\text{-MMT}/NaBH_4$ (Figure 4) suggests that silver-montmorillonite composites are stable against oxidation. The composites were repeatedly analyzed by TEM during five months after their preparation. They were stored in common Eppendorf tubes, in the dark, at room temperature.

The size distribution of silver nanoparticles was quantified using images in the 100 nm scale. About 150 particles were analysed for each sample. As the particles are more or less isometric (Figure 3), their size can be represented by the diameter of a circle with the same area. The sizes were plotted into a histogram with a 1 nm interval to characterize the size distribution of silver nanoparticles (Figure 5). Statistics was calculated on the diameters as well as their logarithms. Generally, if the distribution is plotted against a logarithmic scale, the maxima are closer to a Gaussian curve and the statistical results (Table 1) appear more meaningful than those based on a linear scale.

Table 1. Basal d_{001} spacings of MMT in $Ag\text{-MMT}$ nanocomposites

MMT sample	Reduction procedure	d_{001} / nm
MMT	none	1.22
$Ag^+\text{-MMT}$	none	1.30
$Ag\text{-MMT}$	F-NaOH	1.26
$Ag\text{-MMT}$	F- $NaHCO_3$	1.26
$Ag\text{-MMT}$	F-TEA	1.39
$Ag\text{-MMT}$	$NaBH_4$	1.25

F: Formaldehyde.

The reduction with formaldehyde leads to a wide particle size distribution (3-102 nm) and a lower dispersion on the MMT surface (Figure 3a). The reduction with

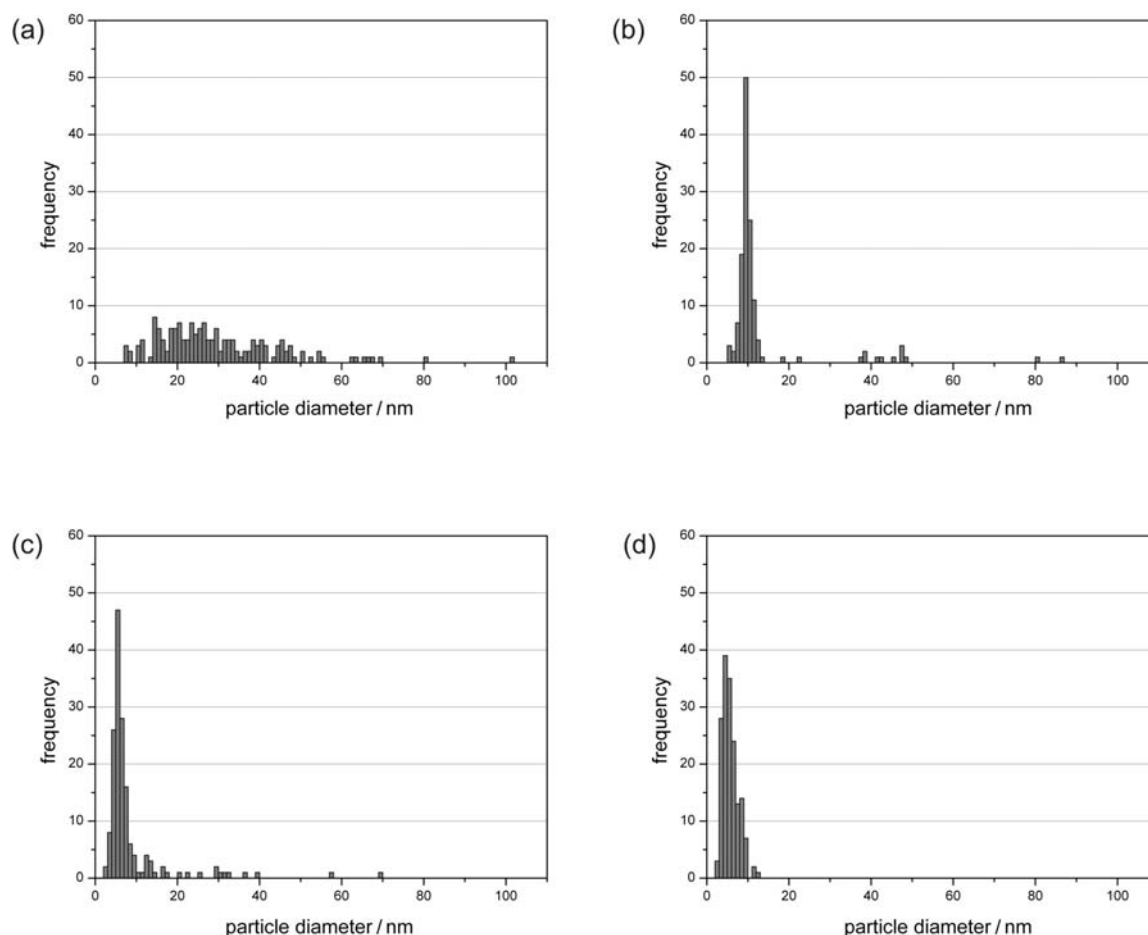


Figure 5. Size distribution histograms of silver particles in silver-montmorillonite nanocomposites prepared by the reduction with: (a) formaldehyde + NaOH, (b) formaldehyde + NaHCO₃, (c) formaldehyde + TEA, and (d) NaBH₄.

NaBH₄ produces silver nanoparticles with sizes from 3 nm to 13 nm (the mean size is 5.4 nm), highly concentrated and evenly dispersed on MMT (Figure 3b). The statistical data are summarised in Table 2. In comparison with other authors,^{4,14,18} the particle size distribution is quite narrow. For the production of particles with a diameter range of several nanometers,¹¹ the method of NaBH₄ has to be further optimised.

The particle size distributions correspond well with the spectral band broadening (Figure 2), except of the sample prepared by reduction with formaldehyde and NaOH.

According to the absorption spectra of this sample, the formation of much smaller particles than those observed by TEM was expected. This discrepancy could be explained by the defect microstructure of silver particles, such as twinning (Figure 3c), likely originated by their fast formation due to the high hydroxide concentration. The existence of particles composed from Ag and Ag₂O should be also expected. These big defective particles absorb light as the aggregates of individual smaller ones welded together; therefore, the absorption band most probably represents these individuals rather than the big particles.

Table 2. Statistics of silver particle size distribution based on logarithms of particle diameter

Reduction procedure	Mean / nm	Standard deviation / nm	Mode / nm	Minimum size / nm	Maximum size / nm	Number of particles
F-NaOH	26.3	1.7	15	7	102	162
F-NaHCO ₃	11.1	1.7	10	5	87	136
F-TEA	7.1	1.8	6	3	70	155
NaBH ₄	5.4	1.4	5	3	13	162

XRD study

The XRD study of MMT, Ag⁺-MMT, and Ag-MMT nanocomposites was carried out to determine the location of silver particles on montmorillonite. From XRD patterns, montmorillonite d_{001} -basal spacings were calculated (Table 1). The initial increase of MMT d_{001} values from 1.22 nm for MMT to 1.30 nm for Ag⁺-MMT confirms the intercalation of silver ions into the interlayer space of montmorillonite. Silver ions intercalation into MMT has been already observed by the increase of d_{001} values as well as by the release of interlayer cations.²

The presence of montmorillonite 001 basal diffractions (Figure 4) indicates that MMT retains its layered structure after the reduction. Silver nanoparticles, due to their size ≥ 3 nm (see Table 2), cannot be located in the interlayer space and, therefore, are placed on the montmorillonite outer surface as shown on TEM micrographs. The MMT interlayer spacing is occupied by sodium or TEA cations compensating the negative layer charge, and this is documented by montmorillonite 001 diffractions (Figure 4) and d_{001} values (Table 1).

Conclusions

In this study, silver-montmorillonite nanocomposites were prepared. The effect of the different reducing agents, such as borohydride and formaldehyde with several alkaline reagents, on the dispersity and size of silver particles supported on montmorillonite surface was demonstrated. The reduction with borohydride produced evenly dispersed silver nanoparticles with sizes ranging from 3 nm to 13 nm, while formaldehyde gave rise to particles from 3 nm to 100 nm. The contents of Ag in Ag-MMT were equal to 2.4 wt% and 5.3 wt% by the use of NaBH₄ and formaldehyde, respectively, depending on Ag particle size. In addition, Ag₂O particles were also found due to the incomplete reduction of Ag₂O by formaldehyde.

In future studies, we intend to improve the reduction procedure, by which we could prepare silver particles with the size on demand. Silver-montmorillonite nanocomposites will be further tested as catalysts and luminescent materials possibly applicable as nanosensors.

Acknowledgments

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